Oxygen-Isotope, X-Ray-Diffraction and Scanning-Electron-Microscope Examinations of Authigenic-Layer-Silicate Minerals from Mississippian and Pennsylvanian Sandstones in the Michigan Basin

By K.F. Zacharias, D.F. Sibley, D.B. Westjohn, and T.L. Weaver

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### **CONVERSION FACTORS AND ABBREVIATIONS**

Multiply	Ву	To obtain	
meter (m)	3.281	foot	
liter (L)	3.785	gallon	
gram (g)	0.002205	pound	

Temperature is given in degrees Celsius (°C), which can be converted to degrees Fahrenheit (°F) by use of the following equation:

$$F = 1.8(^{\circ}C) + 32$$

Abbreviations related to water quality and to isotopic composition of rock-core samples: Dissolved-solids concentration of water is given milligrams per liter (mg/L). Milligrams per liter is a unit expressing the concentration of chemical constituents in solution as weight (milligrams) of solute per unit volume (liter) of water. For concentrations less than 7,000 mg/L, the numerical value is the same as for concentrations in parts per million. Oxygen-isotope composition of rock-core samples is expressed as per mil (parts per thousand) differences in the measured isotopic ratios of the sample to Standard Mean Ocean Water (SMOW). The unit  $\delta^{18}$ O is the standard expression of the ratio of  $\delta^{18}$ O to  $\delta^{16}$ O.

### Other Abbreviations:

EDS	Energy dispersive spectroscopy
RASA	Regional Aquifer-System Analysis
SEM	Scanning electron microscopy
XRD	X-ray diffraction

# OXYGEN-ISOTOPE, X-RAY-DIFFRACTION, AND SCANNING-ELECTRON-MICROSCOPE EXAMINATIONS OF AUTHIGENIC-LAYER-SILICATE MINERALS FROM MISSISSIPPIAN AND PENNSYLVANIAN SANDSTONES IN THE MICHIGAN BASIN

By K.F. Zacharias, D.F. Sibley, D.B. Westjohn, and T.L. Weaver

#### **ABSTRACT**

Oxygen-isotope compositions of authigenic-layer silicates (<2-micrometer fraction) extracted from Mississippian and Pennsylvanian sandstones in the Lower Peninsula of Michigan were determined. Petrographic and scanning-electron-microscope examinations, and X-ray diffractograms show that chlorite and kaolinite are the most common authigenic-layer silicates in Mississippian sandstones. The range of oxygen-isotope compositions of chlorite and kaolinite are +10.3 to +11.9 and +12.9 to +19.3 parts per thousand (per mil) (relative to Standard Mean Ocean Water), respectively. Kaolinite is the only authigenic-layer silicate common in Pennsylvanian sandstones (illite and chlorite are minor authigenic phases); isotopic compositions of kaolinite range from +16.8 to +19.0 per mil.

### INTRODUCTION

Oxygen-isotope compositions of authigenic-layer silicates have been used in previous investigations to interpret compositional changes of pore fluids during basin evolution, as well as to interpret corresponding temperature regimes of sandstone reservoirs during mineral diagenesis (Longstaffe, 1986; Longstaffe, 1984; Longstaffe and Ayalon, 1987). The paragenetic sequence of authigenic minerals in sandstones of Mississippian and Pennsylvanian age in the Michigan Basin in the Lower Peninsula of Michigan has been identified (Westjohn and others, 1991). Layer silicates observed include, in order of deposition, early chlorite, kaolinite, and late-stage illite, which was the last authigenic mineral to precipitate. The same sequence of authigenic minerals was observed in Mississippian and Pennsylvanian sandstones that contain ground water having a large range of oxygen-isotope compositions (-15.7 to -1.8 per mil) and dissolved-solids concentrations (189 to 297,000 mg/L) (Dannemiller and Baltusis, 1990). It is unknown whether mineral phases are in isotopic equilibrium with pore water in sandstone aquifers. Knowledge of oxygen-isotope compositions of authigenic-layer silicates is needed to evaluate potential rock-water interactions.

Investigators with the U.S. Geological Survey's Michigan Basin Regional Aquifer-System Analysis program sampled Mississippian and Pennsylvanian sandstones from collections of diamond-drill cores to obtain information on authigenic-layer silicates in sandstones in the Michigan Basin. The suite selected for mineralogical and isotopic analyses includes the Marshall Sandstone of Mississippian age (18 samples, depths of 22 to 1,365 ft) and the Grand River and Saginaw Formations of Pennsylvanian age (8 samples, depths of 63 to 136 ft).

The purpose of this report is to publish oxygen-isotope data of authigenic chlorite and kaolinite extracted from Mississippian sandstones and authigenic kaolinite extracted from Pennsylvanian sandstones. The primary goal of the investigation is to provide solid-phase-isotope data for sandstones sampled from areas of the basin where dissolved-solids concentrations and isotopic compositions of ground water span the range known to exist in the basin.

# OXYGEN-ISOTOPE, X-RAY-DIFFRACTION, AND SCANNING-ELECTRON-MICROSCOPE EXAMINATIONS

Mississippian and Pennsylvanian sandstones are bedrock aquifers in the Michigan Basin. Samples from these units were selected and prepared for scanning-electron-microscope (SEM) examinations, isotopic analyses, and X-ray-diffraction (XRD) analyses. The samples were selected from collections of cores (Michigan State University and University of Michigan core laboratories; U.S. Geological Survey core collection) drilled as part of hydrocarbon-exploration or hydrogeologic investigations. The locations of drill-hole sites are shown in figure 1 and listed in table 1 (all tables are at the end of the report).

Oriented-specimen mounts were prepared for XRD analyses according to methods outlined by Jackson (1979). As many as eight treatments are necessary to identify different layer-silicate minerals. These treatments include potassium saturation at 25, 300, and 550°C; magnesium saturation and ethylene glycol solvation; glycerol solvation; hydrazine intercalation; High Gradient Magnetic Separation, and deionized-water rinsing. Layer-silicate minerals were identified on the basis of characteristic basal reflections. The XRD data are summarized in table 2.

The High Gradient Magnetic Separation method of Tellier and others (1988) was used to concentrate paramagnetic (chlorite) and diamagnetic (kaolinite) minerals for isotopic analyses. Oxygen was extracted from kaolinite and chlorite separates for mass-spectrographic analyses by use of the bromine pentaflouride method of Clayton and Mayeda (1963). Oxygen-isotope compositions of authigenic chlorite and kaolinite extracts from Mississippian sandstones range from +10.3 to +11.9 and +12.9 to +19.3 per mil, respectively. Oxygen-isotope compositions of kaolinite extracts from the Pennsylvanian sandstones range from +16.8 to +19.0 per mil. Chlorite and illite are present in Pennsylvanian sandstones in insufficient quantities for isotopic analyses. The isotopic data are summarized in table 3.

SEM examinations of samples were combined with energy-dispersive-spectroscopy analyses to identify authigenic-layer-silicate minerals. Authigenic-layer-silicate minerals in Mississippian sandstones are chlorite, kaolinite, and illite (table 4). Paragenetic relations of authigenic-layer-silicate minerals were identified by use of petrographic and SEM examinations. Textural criteria were then used to identify growth relations among all authigenic minerals in the suite of sandstone samples (Westjohn and others, 1991). The paragenetic sequence of authigenic-layer silicates in Mississippian and Pennsylvanian sandstones is, in order of deposition, chlorite, kaolinite, and illite.

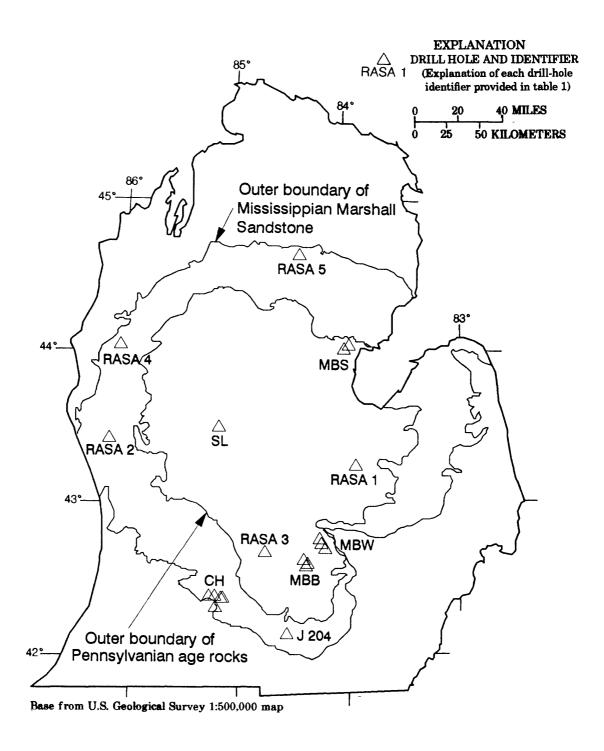


Figure 1.--Lower Peninsula of Michigan and locations of drill holes. (Geologic contacts modified from Martin, 1955.)

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**DATA TABLES** 

Table 1.--Chemical and isotopic composition of ground water and locations of drill holes in the Michigan Basin, Lower Peninsula of Michigan

Drill-hole identifier: Prefix abbreviations indicate location. J204, Jackson County; CH, Battle Creek area, Calhoun County; RASA 1, Montrose area, Genesee County; RASA 2, Holton area, Muskegon County; RASA 3, Benton area, Eaton County; RASA 4, Sauble area, Lake County; RASA 5, Crawford County; SL, Six Lakes, Montcalm County; MBB, Bunkerhill area, Ingham County; MBS, Standish area, Arenac County; MBW, Williamston area, Ingham County.

Dissolved solids (mg/L): Measured dissolved-solids concentration of ground water, in milligrams per liter.

 $\delta^{18}O$  of ground water: Measured oxygen-isotope composition of ground water.  $\delta^{18}O$  is expressed as the relative difference in parts per thousand (per mil) between the  $^{18}O/^{16}O$  ratio in a sample and the ratio in Standard Mean Ocean Water (SMOW).

Location: Location of drill hole in township and range subdivision system. Sec #, section number; 1/4 sec, quarter section; T, township.

Drill-ho	le	Dissolved	δ <sup>18</sup> O of			Location		
identifi	er	solids (mg/L)	ground water	Sec#	1/4 of	1/4 sec	T	Range
					1/4 sec			_
			Mississippia	ın sandstor	nes			
*J 204	8	350	-9.5	13	SE	NW	3S	2W
*CH 101	$\otimes$	350	-10.0	4	NW	NW	2S	7W
*CH 105	$\otimes$	350	-10.0	33	NW	SE	1S	7W
*CH 107	$\otimes$	350	-10.0	5	NW	NE	2S	7W
*CH 130	$\otimes$	350	-10.0	32	SE	SE	2S	7W
*CH 139	$\otimes$	350	-10.0	32	SE	SE	2S	7W
RASA 1		98,700	-7.8	10	SE	SE	9N	5E
RASA 2		45,600	-12.8	30		NE	12N	15W
RASA 3		4,500	-8.2	20	sw	SE	3N	4W
RASA 4		81,400	-10.3	23			19N	14W
RASA 5		1,930	-13.2	12	SW	SW	25N	2W
*SL <sup>1</sup>		$\alpha_{207,000}$	$\beta_{+.5}$	9	NE	NW	12N	7W
			Pennsylvani	an sandsto	nes			
*MBB2	8	450	-9.0	16	NE	NW	1N	2E
*MBB4	$\otimes$	450	<b>-9</b> .0	27	NE	NW	1N	1E
*MBB5	$\otimes$	450	<b>-</b> 9.0	12	NW	sw	1N	1E
*MBS2	$\otimes$	1,800	-10.0	6	SW	SE	18N	5E
*MBS3	$\otimes$	500	-11.0	6		SW	18N	5E
*MBW4	$\otimes$	330	-10.0	8	NE	NE	3N	2E
*MBW5	$\otimes$	480	-10.0	1	SE	SE	3N	1E
*MBW6	8	630	-10.0	7	NE	NW	3N	1E

<sup>\*,</sup> denotes drill holes for which dissolved-solids concentrations and oxygen-isotope compositions of ground water are approximated from the measured values of ground water from nearby wells. ⊗, data from Dannemiller and Baltusis, 1990; α, data from Western Michigan University, 1981; β, data from Clayton and Mayeda, 1963.

<sup>1/</sup>Michigan Department of Natural Resources, Oil and Gas Permit 31497.

Table 2.-X-ray-diffraction analyses of authigenic-layer-silicate minerals from Mississippian and Pennsylvanian sandstones in the Michigan Basin, Lower Peninsula of Michigan

Drill-hole identifier: Prefix abbreviations indicate location. J204, Jackson County; CH, Battle Creek area, Calhoun County; RASA 5, Crawford County; SL, Six Lakes, Montcalm County.

Treatments: Treatments applied to the < 2-micrometer fraction of samples. DI, deionized-water rinsing (air dried); GLY, glycerol solvation; HG, High Gradient Magnetic Separation; HZ, hydrazine intercalation; K25, potassium saturation at 25°Centigrade; K300, potassium saturation at 300°Centigrade; K550, potassium saturation at 550°Centigrade; MG, magnesium saturation and ethylene-glycol solvation.

Mineral: Minerals identified on the basis of characteristic basal reflections. C, chlorite; K, kaolinite; I, illite; S, smectite; I/S, illite/smectite interlayer; C/K, chlorite and (or) kaolinite (unable to differentiate, basal reflections overlap); I/K, illite and (or) kaolinite (unable to differentiate, basal reflections overlap).

I/Imax: I is the relative intensity of basal reflections (in percent), the largest peak, Imax, is 100 percent.

Basal reflections: Å, angstroms; -, no response at this wavelength (mineral not identified).

Drill-hole	Depth	Treat-	Mineral				Basal			
identifier	(feet)	ment	I/Imax				reflections			
				18Å	14Å	10Å	7Å	5Å	3.5Å	3.3Å
J 204	25	DI	Mineral	-	С	I	C/K	I	C/K	I
			I/Imax	-	5	18	100	5	70	25
		GLY	Mineral	-	С	I/S	C/K	I	C/K	I
			I/Imax	-	15	25	100	5	55	10
		HG	Mineral	-	-	I	K	I	K	I
			I/Imax	-	-	3	100	I	80	10
		HZ	Mineral	-	-	I/K	-	I	K	I
			I/Imax	-	-	100	-	3	70	10
	33	$\mathbf{DI}$	Mineral	-	С	I	C/K	I	C/K	I
			I/Imax	-	10	15	100	5	60	20
		HG	Mineral	-	-	I	K	I	K	I
52			I/Imax	-	-	8	100	5	70	25
	52	DI	Mineral	-	C	I	C/K	I	C/K	I
			I/Imax	-	5	20	100	5	50	25
		HG	Mineral	-	-	I	K	I	K	I
			I/Imax	-	-	15	100	5	60	20
	61	DI	Mineral	-	C	I	C/K	I	C/K	I
			I/Imax	-	5	10	100	5	70	15
		HG	Mineral	-	•	I	K	I	K	I
			I/Imax	-	-	10	100	5	70	15
		HZ	Mineral	-	-	I/K	_	I	K	I
			I/Imax	-	-	100	-	5	70	20
		K25	Mineral	-	С	I	C/K	I	C/K	I
			I/Imax	-	5	20	100	5	70	20
		K300	Mineral	-	С	I	C/K	I	C/K	I
			I/Imax	-	5	20	100	10	60	15
		K550	Mineral	-	C	I	С	I	С	I
			I/Imax	-	50	100	10	20	2	40
		GLY	Mineral	-	С	I	C/K	I	C/K	I
			I/Imax	-	10	10	100	5	80	20
		HG	Mineral	-	-	I	K	I	K	I
			I/Imax	_	-	12	100	5	40	10

Table 2.--X-ray-diffraction analyses of authigenic-layer-silicate minerals from Mississippian and Pennsylvanian sandstones in the Michigan Basin, Lower Peninsula of Michigan--Continued

Drill-hole identifier	Depth (feet)	Treat- ment	Mineral I/Imax				Basal reflections			
			•	18Å	14Å	10Å	7Å	5Å	3.5Å	3.3Å
J 204	61	HZ	Mineral	-	-	I/K	_	I	K	I
			I/Imax	-	-	100	-	5	60	10
	81	DI	Mineral	_	C	I	C/K	I	C/K	I
			I/Imax	-	10	15	100	5	70	30
		HG	Mineral	-	-	I	K	I	K	I
			I/Imax	-	-	5	100	5	55	10
CH 101	22	DI	Mineral	-	С	I	C/K	I	C/K	I
			I/Imax	-	10	15	100	5	65	25
		GLY	Mineral	-	С	I	C/K	I	C/K	I
			I/Imax	-	5	20	100	5	50	20
		HG	Mineral	_	-	I	K	I	K	I
			I/Imax	-	-	10	100	5.	60	25
		HZ	Mineral	_		ľК	-	Ī	K	I
			I/Imax	_	-	100	-	10	50	20
	60	DI	Mineral	_	С	I	C/K	I	C/K	I
		٥.	I/Imax	_	20	30	100	10	55	40
	90	DI	Mineral	_	C	I	C/K	I	C/K	I
	,,,	<b>D</b> .	I/Imax	-	15	30	100	15	100	35
CH105 60	60	DI	Mineral	_	С	I	C/K	I	C/K	I
	00	Di	I/Imax	_	15	25	100	10	80	35
	90	DI	Mineral	_	C	I	C/K	I	C/K	I
	70	Di	I/Imax	_	20	10	100	10	60	30
	120	DI	Mineral	_	C	I	C/K	I	C/K	I
	120	<b>D</b> 1	I/Imax	-	25	25	100	15	70	35
CH 107	25	DI	Mineral	_	С	I	C/K	I	C/K	I
011107	20	٠.	I/Imax	_	15	30	100	15	100	35
		GLY	Mineral	_	C	I	C/K	I	C/K	I
		0.51	I/Imax	_	30	25	100	15	65	40
		HG	Mineral	- -	-	I	K	I	K	I
		110	I/Imax		-	15	100	5	60	30
		HZ	Mineral	-	-	I/K	-	I	K	I
		112	I/Imax	-	-	100	-	10	40	20
	90	DI	Mineral	-	Ċ	I	C/K	I	C/K	20 I
	90	Di	I/Imax	-	15	25	100	15	65	35
	120	DI	Mineral	•	C					
	120	DI		-	-	I	C/K	I	C/K	I
	107	DI	I/Imax	-	20	25	100	20	80	40
	197	DI	Mineral	-	C	I	C/K	I	C/K	I
			I/Imax	-	10	25	100	15	60	40
CH 130	60	DI	Mineral	-	C	I	C/K	I	C/K	I
			I/Imax	-	30	35	100	20	70	35
	90	DI	Mineral	-	С	I	C/K	I	C/K	I
			I/Imax	-	15	30	100	15	60	35
	120	DI	Mineral	-	С	I	C/K	I	C/K	I
			I/Imax	-	<b>2</b> 0	40	100	20	80	40
CH 139	60	DI	Mineral	-	C	I	C/K	I	C/K	I
			I/Imax	-	10	25	100	20	80	30

Table 2.--X-ray-diffraction analyses of authigenic-layer-silicate minerals from Mississippian and Pennsylvanian sandstones in the Michigan Basin, Lower Peninsula of Michigan--Continued

Drill-hole identifier	Depth (feet)	Treat- ment	Mineral I/Imax				Basal reflections			
identifier	(leet)	ment	rimax -	18Å	14Å	10Å	7Å	5Å	3.5Å	3.3Å
CH 139	90	DI	Mineral	-	С	I	C/K	I	C/K	I
			I/Imax	-	30	40	100	20	80	35
	120	DI	Mineral	_	C	I	C/K	I	C/K	I
			I/Imax	-	20	30	100	20	80	40
RASA 5	514	DI	Mineral	-	С	I	C/K	I	C/K	I
			I/Imax	-	10	15	100	5	65	25
		HG	Mineral	-	-	I	K	I	K	I
			I/Imax	-	-	10	100	5	55	20
		HZ	Mineral	-	-	I/K	-	I	K	I
			I/Imax	-	-	100	-	5	45	15
	524	DI	Mineral	-	C	I	C/K	I	C/K	I
			I/Imax	-	5	15	100	5	20	25
		HG	Mineral	-	-	I	K	I	K	I
			I/Imax	-	-	10	100	5	60	20
		K25	Mineral	-	C	I	C/K	I	C/K	I
			I/Imax	-	5	20	100	5	<b>7</b> 0	20
		K300	Mineral	-	C	I	C/K	I	C/K	I
			I/Imax	-	5	20	100	10	60	20
526		K550	Mineral	-	C	I	C	I	C	I
			I/Imax		50	100	10	20	5	40
		MG	Mineral	S	C	I	C/K	I	C/K	I
			I/Imax	10	15	25	100	5	65	20
	526	DI	Mineral	-	C	I	C/K	I	C/K	I
	<b>D1</b>	I/Imax	_	5	15	100	5	70	20	
		HG	Mineral	_	-	I	K	I	K	I
		110	I/Imax		_	10	100	5	50	20
		HZ	Mineral	=	-	I/K	-	I	K	20 I
		1123	I/Imax	-	-	100	-	5	40	15
SL	1280	DI	Mineral	-	C	I	C/K	I	C/K	I
			I/Imax	-	10	15	100	5	55	25
		GLY	Mineral	-	С	I	C/K	I	C/K	I
			I/Imax	-	10	10	100	5	50	15
		HG	Mineral	-	-	I	K	I	K	I
			I/Imax	-	-	10	100	5	60	20
		HZ	Mineral	-	-	I/K	-	I	K	I
			I/Imax	_	-	100	_	10	40	10
	1286	DI	Mineral	-	С	I	C/K	I	C/K	I
		_	I/Imax	_	10	15	100	10	70	25
		GLY	Mineral	_	C	I	C/K	I	C/K	I
		ODI	I/Imax	_	10	20	100	10	60	20
		HG	Mineral	-	-	I	K	I	K	20 I
		110	I/Imax	_	-	15	100	10	50	
		HZ	Mineral	-	-	<u> ИК</u>				20
		112		•	-		-	I	K	I
	1204	Di	I/Imax	-	-	100	-	10	45	20
	1304	DI	Mineral	-	C	I	C/K	I	C/K	I
		OI W	I/Imax	-	10	20	100	10	60	25
		GLY	Mineral	-	C	I	C/K	I	C/K	I
			I/Imax	-	10	10	100	5	<b>7</b> 0	25

Table 2.--X-ray-diffraction analyses of authigenic-layer-silicate minerals from Mississippian and Pennsylvanian sandstones in the Michigan Basin, Lower Peninsula of Michigan--Continued

Drill-hole	Depth	Treat-	Mineral				Basal			
identifier	(feet)	ment	I/Imax				reflections			
				18Å	14Å	10Å	7Å	5Å	3.5Å	3.3Å
SL	1304	HG	Mineral	-	-	I	K	I	K	I
			I/Imax	-	-	10	100	5	50	30
		HZ	Mineral	-	-	I/K	-	I	K	I
			I/Imax	-	-	100	-	10	40	20
	1306	DI	Mineral	-	C	I	C/K	I	C/K	I
			I/Imax	-	20	25	100	10	70	35
		GLY	Mineral	-	С	I	C/K	I	C/K	I
			I/Imax	-	20	30	100	10	50	40
	1306	HG	Mineral	-	-	I	K	I	K	I
			I/Imax	-	-	10	100	5	60	30
	1318	DI	Mineral	-	С	I	C/K	I	C/K	I
			I/Imax	-	10	20	100	10	55	25
1334		HG	Mineral	-	-	I	K	I	K	I
			I/Imax	-	-	25	100	10	65	40
	1334	DI	Mineral	-	С	I	C/K	I	C/K	I
			I/Imax	-	10	15	100	5	60	30
		GLY	Mineral	-	С	I	C/K	I	C/K	I
			I/Imax	-	5	15	100	5	65	25
		HG	Mineral	-	_	I	C/K	I	C/K	I
			I/Imax	_	_	5	100	5	50	5
		HZ	Mineral	-	-	-	C	-	С	_
			I/Imax	-	-	-	100	-	60	_
	1359	DI	Mineral	-	С	I	C/K	-	C/K	I
			I/Imax	_	10	20	100	5	60	25
		GLY	Mineral	_	Ĉ	I	C/K	Ī	C/K	I
			I/Imax	-	20	25	100	5	60	30
		HG	Mineral	_	-	-	C/K	_	C/K	I
		110	I/Imax	_	_	_	100	_	50	20
		HZ	Mineral	_	_	_	C	_	C	-
		112	I/Imax	_	_	_	100		60	_
	1365	DI	Mineral	_	С	I	C/K	I	C/K	Ī
	1000	21	I/Imax	_	10	15	100	5	55	30
		GLY	Mineral	_	C	I	C/K	I	C/K	I
		0.01	I/Imax	_	20	20	100	10	60	20
		HG	Mineral	-	-	-	C/K	-	C/K	-
		110	I/Imax	_	-	-	100	-	60	-
		HZ	Mineral	_	_	_	100 C	_	C	
		112	I/Imax	-	-	-	100	-	50	-

Table 3.--Oxygen-isotope compositions of kaolinite and chlorite from Mississippian and Pennsylvanian sandstones in the Michigan Basin, Lower Peninsula of Michigan

Drill-hole identifier: Prefix abbreviations indicate location. Mississippian sandstones denoted by J204, CH, RASA 5, and SL prefixes. CH, Battle Creek area, Calhoun County; J204, Jackson County; RASA 5, Crawford County; SL, Six Lakes, Montcalm County. Pennsylvanian sandstones denoted by MBB, MBS, and MBW prefixes. MBB, Bunkerhill area, Ingham County; MBS, Standish area, Arenac County; MBW, Williamston area, Ingham County.

δ<sup>18</sup>O SMOW (‰): Oxygen-isotope compositions, in parts per thousand (per mil), as related to Standard Mean Ocean Water:

by a kaolinite-water equilibrium fractionation factor (Savin and Lee, 1988),  $10^3 \ln \alpha \text{ (kaolinite-water)} = 10.6 (10^3/\text{T}) + 0.42 (10^6/\text{T}^2) -15.337;$ 

or by a chlorite-water equilibrium fractionation factor (Savin and Lee, 1988),  $10^3 \ln \alpha$  (chlorite-water) =  $11.545 + 1.455 (10^3/T) + 4.077 (10^6/T^2) - 0.831 (10^9/T^3) + 0.075 (10^{12}/T^4)$ , where  $\alpha$  is the oxygen isotope fractionation factor, and T is temperature, in degrees centigrade.

Oxygen yield (µmol/mg): Estimate of sample purity. Pure kaolinite yields approximately 17.4 µmol/mg of oxygen, converted to CO<sub>2</sub>; pure chlorite yields approximately µmol/mg of oxygen, converted to CO<sub>2</sub> (\*J.P. Girard, Case Western Reserve University, written commun., 1992).

Size (µm): Size fraction of clay mineral separates used for isotopic analysis, in micrometers.

Minerals analyzed: Minerals extracted for isotopic analysis.

Drill-hole	Depth	$\delta^{18}O$	Yield	Size	Minerals
identifier	(feet)	<b>SMOW</b>	(µmol/mg)	(µm)	analyzed
		(‰)			
		Mississ	sippian sandston	ies	
J204	25	18.19	16.68	1-2	kaolinite
	25	17.51	15.14	0.3-1	kaolinite
	33	17.98	14.58	1-2	kaolinite
	52	18.87	16.80	1-2	kaolinite
	61	18.55	15.73	1-2	kaolinite
	70	18.01	15.14	1-2	kaolinite
	70	17.83	15.10	1-2	kaolinite
	81	12.85	12.14	1-2	kaolinite
CH 101	22	18.16	16.21	1-2	kaolinite
CH 107	25	17.98	15.29	1-2	kaolinite
RASA 5	514	19.00	16.52	1-2	kaolinite
	524	18.91	15.07	1-2	kaolinite
**	524	18.20	14.67	1-2	kaolinite
	526	19.33	16.80	1-2	kaolinite

Table 3.--Oxygen-isotope compositions of kaolinite and chlorite from Mississippian and Pennsylvanian sandstones in the Michigan Basin, Lower Peninsula of Michigan--Continued

		10			
Drill hole	Depth	$\delta^{18}O$	Yield	Size	Minerals
identifier	(feet)	SMOW	(µmol/mg)	(µm)	analyzed
		(‰)			
SL	1280	18.27	15.45	1-2	kaolinite
	1286	18.25	15.69	1-2	kaolinite
	1304	18.20	15.63	1-2	kaolinite
	1306	18.08	15.51	1-2	kaolinite
	1334	10.63	13.45	1-2	chlorite
**	1334	10.33	13.82	1-2	chlorite
	1359	11.21	11.67	1-2	chlorite
**	1359	11.20	13.66	1-2	chlorite
	1365	11.89	11.56	1-2	chlorite
**	1365	11.85	12.14	1-2	chlorite
	· · · · · · · · · · · · · · · · · · ·	Pennsylv	vanian sandstone	es	
MBB2	76	16.81	15.66	1-2	kaolinite
MBB4	64	17.39	15.97	1-2	kaolinite
MBB5	63	17.16	15.61	1-2	kaolinite
MBS2	136	17.10	15.68	1-2	kaolinite
MBS3	64	19.03	15.87	1-2	kaolinite
MBW4	97	17.73	15.69	1-2	kaolinite
MBW5	85	16.91	15.61	1-2	kaolinite
MBW6	97	17.57	15.53	1-2	kaolinite

<sup>\*\*</sup> Denotes duplicate analysis

Table 4.--Scanning-electron-microscope and energy-dispersive-spectroscopy identification of authigenic-layer silicates from Mississippian sandstones in the Michigan Basin, Lower Peninsula of Michigan

Drill-hole identifier: Prefix abbreviations indicate location. J204, Jackson County; CH, Battle Creek area, Calhoun County; RASA 1, Montrose area, Genesee County; RASA 2, Holton area, Muskegon County; RASA 3, Benton area, Eaton County; RASA 4, Sauble area, Lake County; RASA 5, Crawford County; SL, Six Lakes, Montcalm County.

Mineral: A, abundant; x, present, but not abundant; -, not identified.

Drill-hole	Depth		Mineral	
identifier	(feet)	chlorite	kaolinite	illite
J 204	25	•	A	х
	33	-	Α	x
	41	-	Α	x
	52	-	Α	X
	61	X	Α	x
	70	X	Α	x
	82	Α	Α	X
	91	Α	x	x
	101	Α	x	X
CH 101	25	-	Α	-
	41	-	Α	-
	49	-	x	x
	55	-	x	X
	60	X	x	-
	62	-	Α	X
	90	A	-	X
	120	Α	-	x
CH 105	33	-	x	x
	57	-	Α	X
	61	X	-	x
	85	X	-	x
	125	Α	-	x
CH 107	25	-	Α	x
	40	-	Α	X
	62	X	x	X
	88	X	-	x
	120	X	-	X
CH 130	35	-	Α	Α
	46	-	x	-
	56	X	-	X
	90	X	-	X
	111	X	-	x

Table 4.--Scanning-electron-microscope and energy-dispersive-spectroscopy identification of authigenic-layer silicates from Mississippian sandstones in the Michigan Basin, Lower Peninsula of Michigan--Continued

Drill-hole	Depth		Mineral	
identifier	(feet)	chlorite	kaolinite	illite
CH 139	35	-	х	х
	50	-	x	•
	56	X	-	x
	60	X	-	x
	85	X	-	X
	123	Α	-	x
RASA 1	487	-	Α	x
	500	-	Α	x
	520	-	Α	X
RASA 2	432	-	Α	x
	459	X	Α	x
	465	X	Α	x
	475	X	Α	X
	485	X	Α	X
	505	X	Α	x
	525	x	Α	x
RASA 3	490	-	Α	x
	500	X	x	x
	525	A	-	x
	600	Α	-	-
RASA 4	560	-	x	-
	578	-	Α	x
	594	-	x	x
	606	X	X	x
	616	X	X	x
	624	-	-	Α
	632	X	-	x
RASA 5	502	Α	Α	x
	514	Α	x	
	520	Α	Α	Α
	524	Α	x	x
	526	Α	x	x
	531	Α	x	Α
	533	Α	X	x
	587	Α	x	x
	591	Α	-	x
	599	Α	-	x

Table 4.--Scanning-electron-microscope and energy-dispersive-spectroscopy identification of authigenic-layer silicates from Mississippian sandstones in the Michigan Basin, Lower Peninsula of Michigan--Continued

Drill-hole	Depth		Mineral	
identifier	(feet)	chlorite	kaolinite	illite
RASA5	607	Α	-	х
	617	Α	-	Α
SL	1276	-	Α	X
	1280	-	x	X
	1285	-	X	X
	1286	-	Α	Α
	1287	-	Α	Α
	1304	-	Α	Α
	1306	-	Α	X
	1318	X	Α	X
	1330	Α	Α	X
	1334	Α	-	x
	1347	Α		-
	1353	Α	-	x
	1359	Α	-	X
	1365	Α		X